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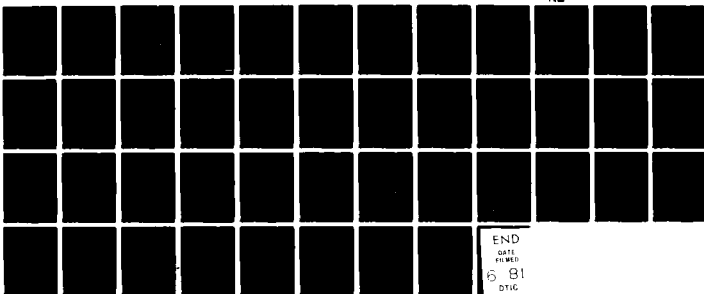
DEVELOPMENT OF ADVANCED KOCITE ELECTROCATALYSTS FOR PHOSPHORIC --ETC(U)

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DEVELOPMENT OF ADVANCED YOCITE ELECTROCATALYSTS FOR
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by
L. E. Welsh, R. W. Leyerle, D. S. Scarlata, M. A. Vanek

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DEVELOPMENT OF ADVANCED KOCITE® ELECTROCATALYSTS FOR
PHOSPHORIC ACID FUEL CELLS

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L. B. Welsh, R. W. Leyerle, D. S. Scarlata, and M. A. Vanek

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ABSTRACT

This report discusses the results of a one-year program (Contract No. DAAK70-79-C-0173) funded by USA-MERADCOM to develop from Kocite® materials, better electrocatalysts for phosphoric acid electrolyte fuel cell applications. These improved electrocatalysts should demonstrate a larger initial catalytic metal surface area, and a better catalytic metal surface area retention during fuel cell operation than present state-of-the-art phosphoric acid electrocatalysts. Kocite electrocatalysts impregnated with platinum and platinum-vanadium alloys were tested. The Kocite electrocatalysts were aged in electrodes potentiostated in H_3PO_4 half cells, and were then analyzed for catalytic metals surface area retention.

Compared with the state-of-the-art platinum electrocatalysts, as represented by a standard Kocite electrocatalyst, the Kocite electrocatalysts impregnated by the techniques used in this study had a better initial platinum surface area. This initial surface area difference appeared to be maintained when the catalysts are aged at 700 mV, but was not maintained when the catalysts were aged at 800 mV. Variations of the alumina substrate and of the posttreatment of the leached Kocite catalyst support did not produce any catalysts with better platinum surface area retention than the standard catalyst. Alloying of vanadium with the platinum did produce Kocite electrocatalysts which maintained their alloy surface area better than the standard catalyst maintained its platinum surface area.

SUMMARY

The results discussed in this report summarize the efforts of a one year program funded by the U.S. Department of Energy through USA-MERADCOM (Contract No. DAAK70-79-C-0173) to develop from Kocite® materials, better electrocatalysts for phosphoric acid electrolyte fuel cell applications. These improved electrocatalysts should demonstrate a larger initial catalytic metal surface area and better catalytic metal surface area retention during fuel cell operation than present state-of-the-art, phosphoric acid electrocatalysts. Thirteen Kocite electrocatalyst materials were prepared during this program and eleven electrocatalysts were tested.

The starting Kocite materials are composite structures consisting of a thin film, semiconducting pyropolymer chemically bonded to the surface of an electrically-insulating, high-surface-area, refractory support. While Kocite materials themselves can be used as catalyst supports, for use in H_3PO_4 fuel cells, the refractory substrate is leached from the composite structure to leave a high-surface-area, carbonaceous support material. This support is then impregnated with either platinum or platinum and vanadium.

The Kocite electrocatalysts were aged in PTFE-bonded electrodes potentiostated in H_3PO_4 , and then analyzed to determine their catalytic metal surface area retention. The testing was done in two parts, an initial screening of the standard catalyst and eight catalyst variations, and a subsequent more extensive testing of the two most promising catalysts. In Part 1, aging tests were carried out for 100 and 500 hours at $190^\circ C$ with the Kocite electrodes potentiostated at 800 mV (versus a normal hydrogen electrode). In Part 2, two Pt-V alloy catalysts were further tested with a greater number of cells at the same aging conditions. Selected catalysts were also aged at 700 mV.

Several impregnation variations were made on a master batch of support material, a leached Kocite material prepared from Hydral 705 alumina substrate. A catalyst prepared with platinum diamine dinitrite was used as the standard catalyst. This standard Kocite catalyst formulation was developed under a previous MERADCOM contract¹ and was comparable to commercial state-of-the-art fuel cell electrocatalysts. Impregnation variations were made with a previously developed UOP experimental impregnation and an impregnation done by an outside company. After aging for 100 and 500 hours potentiostated at 800 mV, these three catalysts had the same platinum surface area retention, about 55 m²/g. This indicates that at 800 mV the impregnation variations did not have a significant effect on the platinum surface area retained after aging. However, after 500 hours at 700 mV the catalyst impregnated by an outside company retained a higher platinum surface area compared to the standard catalyst. The catalyst prepared using a UOP experimental impregnation method was not tested at 700 mV.

Variations were made in the leached Kocite supports, both by posttreatment of the master support batch and by use of a support made using an Alon alumina substrate. The catalysts made from a support posttreated at 2500°C showed poor retention of their platinum loading after 500 hours. A similar result was obtained for the catalyst made from the support using the Alon substrate. A catalyst made from a support that was partially oxidized before impregnation did not appear to have any improved platinum surface area retention over the standard catalyst.

Three catalysts were further impregnated with vanadium to produce platinum-vanadium alloy catalysts. The catalyst produced from the heat treated support did not retain platinum well. The other two catalysts were made from the master batch support with either the UOP experimental or the outside

company impregnations. These latter catalysts had an alloy surface area retention of about $65 \text{ m}^2/\text{g}$, which was about $10 \text{ m}^2/\text{g}$ higher than the platinum surface area retention of the standard pure-platinum catalyst.

Compared with the state-of-the-art platinum electrocatalyst, as represented by the standard catalyst, the catalysts impregnated with either the UOP experimental impregnation or the impregnation by the outside company had better initial platinum surface areas. This initial surface area difference appeared to have been maintained when the catalysts are aged at 700 mV, but was not maintained when the catalysts are aged at 800 mV. Variations of the alumina substrate and of the posttreatment of the leached Kocide support did not produce any catalysts with better platinum surface area retention than the standard catalyst. Alloying of vanadium with the platinum did produce catalysts which maintained their alloy surface area better than the standard catalyst.

I. INTRODUCTION

1.1 Objectives

The objectives of this program were to develop from Kocite^{*} materials, better electrocatalysts for phosphoric acid fuel cell applications. These improved electrocatalysts should demonstrate a larger initial catalytic metals surface area, and better catalytic metal surface area retention during fuel cell operation than present state-of-the-art, phosphoric acid electrocatalysts. To accomplish these objectives, several alternative preparative methods for electrocatalysts made from Kocite materials were explored to determine whether these formulations yielded improved electrocatalysts. Thirteen platinum and platinum-vanadium electrocatalysts were prepared by different techniques. Eleven of these were aged in PTFE-bonded electrodes in electrochemical half cells to determine the extent of their platinum and Pt-V alloy surface area retention under fuel cell operating conditions. This report summarizes the results obtained during this program.

1.2 Background

The program discussed here followed an evaluation of the performance of platinum-impregnated leached-Kocite electrocatalysts in fuel cell electrodes for phosphoric acid electrolyte fuel cells completed for USA-MERADCOM

* Kocite is a registered trademark of UOP Inc.

under contract number DAAK53-76-C-0014.¹ During that program, state-of-the-art catalyst materials were developed and tested in model fuel cells. As a result of the promising initial data obtained during that program, UOP undertook a concurrent contract with the Electric Power Research Institute (RP-1200-3) to study the structural and platinum sintering stability of Kocite electrocatalysts under fuel cell conditions.² In 1979 the US Department of Energy funded the present effort through the USA-MERADCOM to produce and test Kocite electrocatalysts with improved stability.

Kocite materials are proprietary materials of UOP Inc. and are composite structures consisting of a thin film semiconducting pyropolymer chemically bonded to the surface of an electrically-insulating, high-surface-area, refractory substrate. The materials used to produce Kocite can vary widely, but commonly include gamma alumina as the refractory substrate and hydrocarbons as the pyrolyzable material or pyropolymer precursor. The pyrolysis temperatures are commonly in the range of 400 to 1000°C. For use in H_3PO_4 fuel cells, the refractory substrate is leached from the composite to leave a high-surface-area, carbonaceous support material, which is impregnated with platinum.

The support structure and surface chemistry, and the initial catalytic metal surface area were thought to be the most critical parameters determining Kocite electrocatalyst stability. For the electrocatalysts tested during this program, changes were made in these parameters by varying the process conditions used to prepare the supports, the posttreatments of the

¹L. B. Welsh and R. W. Leyerle, Optimization of Pt-Doped Kocite® Electrodes in H_3PO_4 Fuel Cells, MERADCOM Contract DAAK53-76-C-0014, Final Technical Report, May, 1979.

²L. B. Welsh, R. W. Leyerle, D. S. Scarlata, and M. A. Vanek, Stability of Kocite® Electrocatalyst in Phosphoric Acid Fuel Cells, Electric Power Research Institute Contract RP-1200-3, Final Report, July, 1980.

support before impregnation, and the impregnation techniques. All catalysts were impregnated at a nominal 10 wt-% platinum level and several catalysts were also impregnated at a nominal 0.8 wt-% vanadium level to prepare platinum-vanadium alloy catalysts.

II. EXPERIMENTAL PROCEDURES

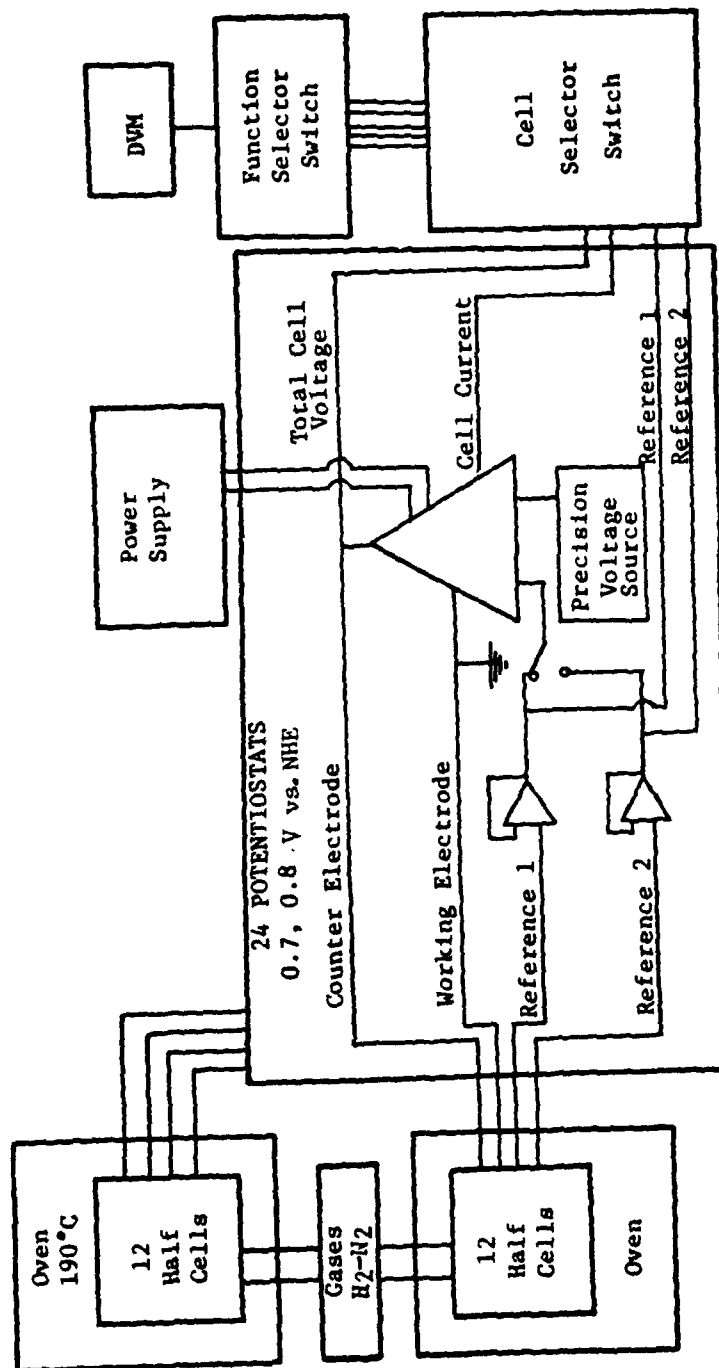
2.1 Electrocatalyst Aging Apparatus

The Kocite electrocatalysts were aged in electrodes potentiostated in H_3PO_4 electrolyte to determine their platinum and platinum-vanadium alloy surface area retention. A test facility was used to age 24 Kocite cathodes in separate electrochemical half cells, each controlled by individual potentiostats. Figure 1 displays a schematic of the aging facility. The main components of this facility are the electrochemical cells, two temperature controlled ovens, and the supporting monitor and control electronics.

Each electrochemical cell contained a Kocite cathode (working electrode), a platinum gauze counter electrode, and one Pd:H reference electrode. The voltage of each cathode was fixed by a separate potentiostat consisting of a simple operational-amplifier-driven current source controlled by the reference electrode voltage.

The reference electrodes consisted of a palladium disk sealed at the end of a tube dipping into the electrolyte. A slow flow of a hydrogen-nitrogen gas mixture was circulated inside the tube. The disks were 7 mm in diameter and 0.1 mm thick with a platinum wire lead spot welded on the gas side. The Pd disk was sealed in a threaded PTFE fitting with Viton washers. The fitting connected to a quartz tube which was sealed at the top to the Pt lead wire and gas tubes. The Pd electrodes were calibrated against a Pt: bubbling H_2 normal hydrogen electrode (NHE) in H_3PO_4 at the temperature used for the catalyst aging tests.

Figure 1. Schematic of the Kocite Electrocatalyst Aging Test Facility



The counter electrode was a piece of platinum mesh held above the working electrode by the PTFE cell body. As the electrolyte, reagent grade H_3PO_4 was used after purification with H_2O_2 and concentration to 102 wt-% H_3PO_4 .

2.2 Kocite PTFE-Bonded Electrodes

The catalysts were incorporated into PTFE-bonded electrode structures. The PTFE content of 10 wt-% was chosen to provide both adequate structural integrity in the long term aging tests and the required hydrophilic electrode structure to insure proper electrocatalyst wetting by the electrolyte. The catalyst powder was slurried together with DuPont's "Teflon 6" PTFE dry powder in heptane. After solvent evaporation, the resulting paste was rolled into a bonded sheet, ~2 mm thick. 40 mm diameter disks were cut from the sheet, and gold wire leads and tantalum screens were then spot welded around the periphery. The disks contained 0.8 to 1 g of catalyst.

2.3 Kocite Electrode Test Conditions

The aging tests were divided into two parts. In Part 1, four cells containing the standard catalyst were aged at 190°C for 100 and 500 hours potentiostated at 800 mV. Two cells containing the catalyst variations were aged under the same conditions. In addition, cells containing the standard catalyst and one catalyst variation were aged at 700 mV to determine the effect of less severe aging conditions.

As a result of the initial aging tests, two catalysts were selected for further testing in Part 2. The two catalysts were aged in cells at 190°C for 100 and 500 hours potentiostated at 700 or 800 mV. Five cells of each catalyst were aged at each condition.

2.4 Kocite Electrocatalyst Analyses

The Kocite electrocatalysts were analyzed for the percentage of C, O, H, Pt, and P present, and selected catalysts were also analyzed for the percentage of Al and V present. The C, O, and H were measured by a standard micropyrolysis technique, Pt was measured spectrophotometrically and by X-ray fluorescence, and V, P, and Al were measured by atomic absorption spectrometry. Measurements of the leached Kocite support pore volume distribution were made by nitrogen desorption on a Micromeretics 2500 automated adsorption apparatus.

The platinum surface areas of fresh and aged catalysts, expressed per gram of platinum, were measured by analyzing the line broadening of the platinum X-ray diffraction peaks. Only a fraction of the platinum particles effectively contribute to this line, as many platinum crystallites are so small that their contributions are smeared out and become part of the background. The agglomerated or measureable fraction is composed of the platinum particles with diameters larger than ~2.0 nm. The average particle size of the agglomerated fraction is calculated from the halfwidth of the diffraction line assuming spherical platinum particles. The platinum surface area was calculated by assuming that any unagglomerated platinum was in particles of 2.0 nm diameter, corresponding to a surface area of 140 m²/g. This technique, therefore, limits the maximum calculated surface

area to $140 \text{ m}^2/\text{g}$. This is a conservative technique which underestimates the surface area for samples with small agglomerations, while being more accurate for samples with higher agglomerations. The platinum surface area, S , was calculated by summing the surface area of the unagglomerated fraction with the surface area derived from the measured average particle size of the agglomerated fraction, or

$$S = \left(140 \frac{\text{m}^2}{\text{g}}\right) (1 - \text{Agg}) + \left(140 \frac{\text{m}^2}{\text{g}}\right) (\text{Agg}) \left(\frac{2.0 \text{ nm}}{d}\right)$$

where Agg is the fraction agglomerated and d is the average particle diameter in nm of the agglomerated particles.

For the X-ray analysis of the Pt-V alloy catalysts, the surface area was expressed per gram of alloy, necessitating a correction for alloy density. An additional correction was made to account for the difference in the X-ray form factor between the pure platinum catalyst used as an X-ray standard and the alloy. The solid solution composition was used to calculate the correction.

All platinum or alloy surface areas have been corrected for any platinum or vanadium loss during aging, and are adjusted to the initial metals content.

III. KOCITE ELECTROCATALYST CHARACTERIZATION

Thirteen batches of Kocite electrocatalyst and one non-Kocite electrocatalyst were prepared during this program. Table I lists the electrocatalysts and their methods of preparation. Catalysts labeled with a "b" are Pt-V alloy catalysts. Catalysts 3b-1, 6b-1, and 8b-1 were prepared from portions of Catalysts 3a, 6a, and 8a, respectively, by an additional vanadium impregnation. Catalysts 3b-2 and 8b-2 were prepared to duplicate Catalysts 3b-1 and 8b-1 so that they could be retested. Table II summarizes the preparation conditions of the Kocite support materials. Table III lists the analytical data obtained on the fresh catalyst samples.

The Kocite materials for this project were prepared by contacting a hydrocarbon vapor stream with a well mixed bed of alumina powder in a high temperature rotary reactor. This procedure deposited a thin film of carbonaceous pyropolymer, a few monolayers thick, on the alumina surface. The carbon film is conformal to the alumina surface and the particle structure is preserved. The alumina was removed by leaching the powder in H_3PO_4 at $160^\circ C$ to leave a high-carbon, high surface area support. This is the same support preparation method used in the previous MERADCOM projects.¹

The primary support material, the "master batch support", was prepared on an Alcoa Hydral 705 alumina. Five separate batches of leached Kocite support were produced using the identical procedure and then mixed well to produce support batch 3971-90L. Samples of this batch were impregnated to produce all catalysts except 2 and 4. Catalysts 2 and 4 were produced on supports based on Cabot's Alon alumina with procedures similar to those used for Alon-based materials in the previous MERADCOM project.¹

Table I

Kocite Electrocatalysts

<u>Catalyst No.</u>	<u>Leached Kocite Support</u>	<u>Post Treatment</u>	<u>Impregnation</u>	<u>Pt Content</u>	<u>V Content</u>
1	Master batch (3971-90L)	-	PDD*	10.36	-
2	Alon-based (3971-98L)	-	PDD	10.21	-
3a	Master Batch (3971-90L)	-	UOP Experimental	9.69	-
3b-1	Master Batch (3971-90L)	-	+ Vanadium**	10.82	0.83
3b-2	Master Batch (3971-90L)	-	+ Vanadium	10.77	0.82
4	Alon-based (3971-104L)	-	UOP Experimental	9.69	-
5	Master Batch (3971-90L)	HNO ₃ Oxidation	PDD	10.18	-
6a	Master Batch (3971-90L)	2500°C	UOP Experimental	9.75	-
6b	Master Batch (3971-90L)	2500°C	+ Vanadium	9.53	0.83
7	Vulcan XC-72R	-	PDD	9.11	-
8a	Master Batch (3971-90L)	-	Outside Company	10.88	-
8b-1	Master Batch (3971-90L)	-	+ Vanadium	10.93	1.08
8b-2	Master Batch (3971-90L)	-	+ Vanadium	11.13	0.96
9	Master Batch (3971-90L)	-	PDD	10.82	-

*Pt(NH₃)₂(NO₂)₂ Platinum diamine dinitrite

**C₅H₅V(CO)₄ Tetracarbonylcyclopentadienylvanadium

Table II

Preparation of Kocite Support Materials

<u>Kocite Batch Number</u>	3971 -18*	3971 -26*	3971 -34*	3971 -40*	3971 -48*	3971 -98	3971 -104
<u>Kocite Preparation</u>							
Substrate	-----Hydral 705-----					Alon	Alon
Particle Size (μm)	0.3	0.3	0.3	0.3	0.3	0.05	0.05
Pyropolymer Precursor	C_6H_6	C_6H_6	C_6H_6	C_6H_6	C_6H_6	C_6H_6	C_6H_6
Pyrolysis Temperature ($^{\circ}\text{C}$)	850	850	848	854	854	905	905
<u>Kocite Characteristics</u>							
Carbon Content (wt-%)	23.69	23.41	22.72	23.67	23.93	37.96	35.60
Resistivity @ 25°C ($\Omega\text{ cm}$)	0.121	0.107	0.113	0.072	0.095	0.035	0.037
Apparent Bulk Density (g/ml)	0.297	0.297	0.295	0.295	0.313	0.133	0.129
Surface Area (m^2/g)	57	53	70	65	57	103	100
Pore Volume (ml/g)	0.08	0.09	0.09	0.08	0.08	0.20	0.20
Average Pore Diameter (nm)	5.6	6.8	5.1	4.9	5.6	7.8	8.0
<u>Leaching Conditions</u>							
Solution	-----85% H_3PO_4 -----						
Time (h)	20	20	20	20	20	20	17
Temperature ($^{\circ}\text{C}$)	184	183	180	183	170	189	185

*After leaching, Kocite batches 3971-18, -26, -34, -40, and -48 were combined to form a master batch, 3971-90L.

Table III

Kocite Electrocatalyst Properties

Catalyst Number	1	2	3a	3b-1	3b-2	4	5	6a	6b	7	8a	8b-1	8b-2	9
Characteristics														
Pt Content (wt-%)	10.36	10.21	9.69	10.82	10.77	9.69	10.18	9.75	9.53	9.11	10.88	10.93	11.13	10.82
V Content (wt-%)	-	-	-	0.83	0.82	-	-	-	0.83	-	-	1.08	0.96	-
Carbon Content (wt-%)	85.57	80.67	82.55	80.79	81.78	81.94	77.25	87.52	86.84	86.25	81.72	83.52	83.90	82.14
Hydrogen Content (wt-%)	1.68	0.72	0.79	0.52	0.69	0.89	1.31	0.62	0.42	0.54	0.97	0.76	0.39	0.85
Oxygen Content (wt-%)	2.49	5.48	3.54	2.29	2.89	3.29	4.1	1.67	2.33	1.94	-	1.22	2.01	2.88
Phosphorus (wt-%)	0.70	0.38	0.64	0.42	0.33	0.77	0.24	0.05	0.05	0.02	0.17	0.20	0.47	0.44
Structure														
Surface Area (m^2/g)	635	309	662	638	630	430	725	153	150	209	648	604	614	603
Pore Volume (ml/g)	1.12	0.78	1.14	1.12	1.11	0.96	1.24	0.32	0.27	0.26	1.15	1.07	1.10	1.12
Avg. Pore Diameter (nm)	7.1	10.1	6.9	7.0	7.0	8.9	6.8	8.4	7.2	5.0	7.1	7.1	7.2	7.4
Pt X-Ray Analysis														
Agglomeration (%)	31	65.2	6.1	69.1	70.6	16.2	51.8	35.6	76.6	32.4	6.8	73.9	93.1	12.8
Avg. Particle Size (nm) of the Agglomerated Fraction	7.0	7.5	5.5	2.9	4.7	2.5	6.9	3.4	3.2	7.3	4.9	3.2	3.4	8.1
Pt Surface Area (m^2/g)	109	73	135	-	-	136	88.5	119	-	107	134	-	-	127
Pt-V Alloy Surface Area (m^2/g)	-	-	-	135	103	-	-	-	123	-	-	125	107	-

The variations made in these batches were primarily variations of support structure, posttreatment, impregnation technique, and catalytic metals composition. Catalyst 1 was used as the standard catalyst material. It was produced on the master support batch with a platinum diamine dinitrite (PDD) impregnation. Catalyst 2 was produced on Alon alumina-based support with the same kind of PDD impregnation. Catalyst 3a was produced on the master batch support with a UOP experimental colloidal impregnation. Catalyst 3b-1 and 3b-2 were produced by vanadium impregnation of Catalyst 3a by the method published by Dr. Phillip Ross of Lawrence Berkeley Laboratory.³ Catalyst 4 was produced with the UOP experimental impregnation on an Alon-based support material. The support for Catalyst 5 was a portion of the master batch posttreated in HNO_3 for 20 hours at 60°C to partially oxidize the surface. The catalyst was produced with a PDD impregnation. The support for Catalyst 6a was a portion of the master batch heat treated at 2500°C . This heat treatment was done by an outside company. Catalyst 6a was impregnated with a UOP experimental method. Catalyst 6b was produced with a vanadium impregnation of Catalyst 6a. Catalyst 7 was produced by a PDD impregnation of Vulcan XC-72R carbon black. Catalyst 8a was produced on the master batch support by platinum impregnation by an outside company. Catalysts 8b-1 and 8b-2 were produced by vanadium impregnation of Catalyst 8a. Catalyst 9 was a PDD impregnated portion of the master batch support which was sent to Energy Research Corp. (3 Great Pasture Road, Danbury, CT) to be tested in trifluoromethanesulfonic acid fuel cells on a different MERADCOM contract.

³P. N. Ross, Jr., Oxygen Reduction on Supported Pt Alloys and Intermetallic Compounds in Phosphoric Acid, U.S. Department of Energy Contract W-7405-ENG-48, March 1980, page 77.

The UOP experimental impregnation method and the outside company's impregnation improved the measured platinum surface area for the fresh catalysts on the master batch support and Alon based support materials compared with the PDD impregnations. On the heat treated material there was improved platinum surface area over PDD impregnated catalysts, but not as good as on the standard base material. On the oxidized support the initial platinum surface area after impregnation with PDD was lower than the platinum surface area of the standard catalyst.

Nominally the Pt-V alloys were prepared at 0.33 V to Pt atomic ratio. The values given in Table III for the alloy agglomeration and surface area are based on the grams of alloy present, corrected for the differing density of the alloys. The alloy agglomerations are larger than the platinum agglomerations of the pure platinum catalysts, but because of the lower density of the alloy, the surface area per gram of alloy is in the same range as for the other catalysts.

The N_2 desorption pore volume distribution (PVD) of the supports was measured. The PVD of the master batch is shown in Figure 2. It is typical of Hydral-based materials with a sharp maximum in the pore distribution at 5.5 nm. The posttreatment of the support for Catalyst 6 reduced the total pore volume and shifted the maximum differential pore volume to a lower pore size, as shown in Figure 3. The Alon-based support for Catalyst 4 has the PVD shown in Figure 4. The oxidation of the support for Catalyst 5 caused no change in the shape of the PVD.

Figure 2
Normalized Pore Volume Distribution of the Master Support Batch
of Leached Kocite Material

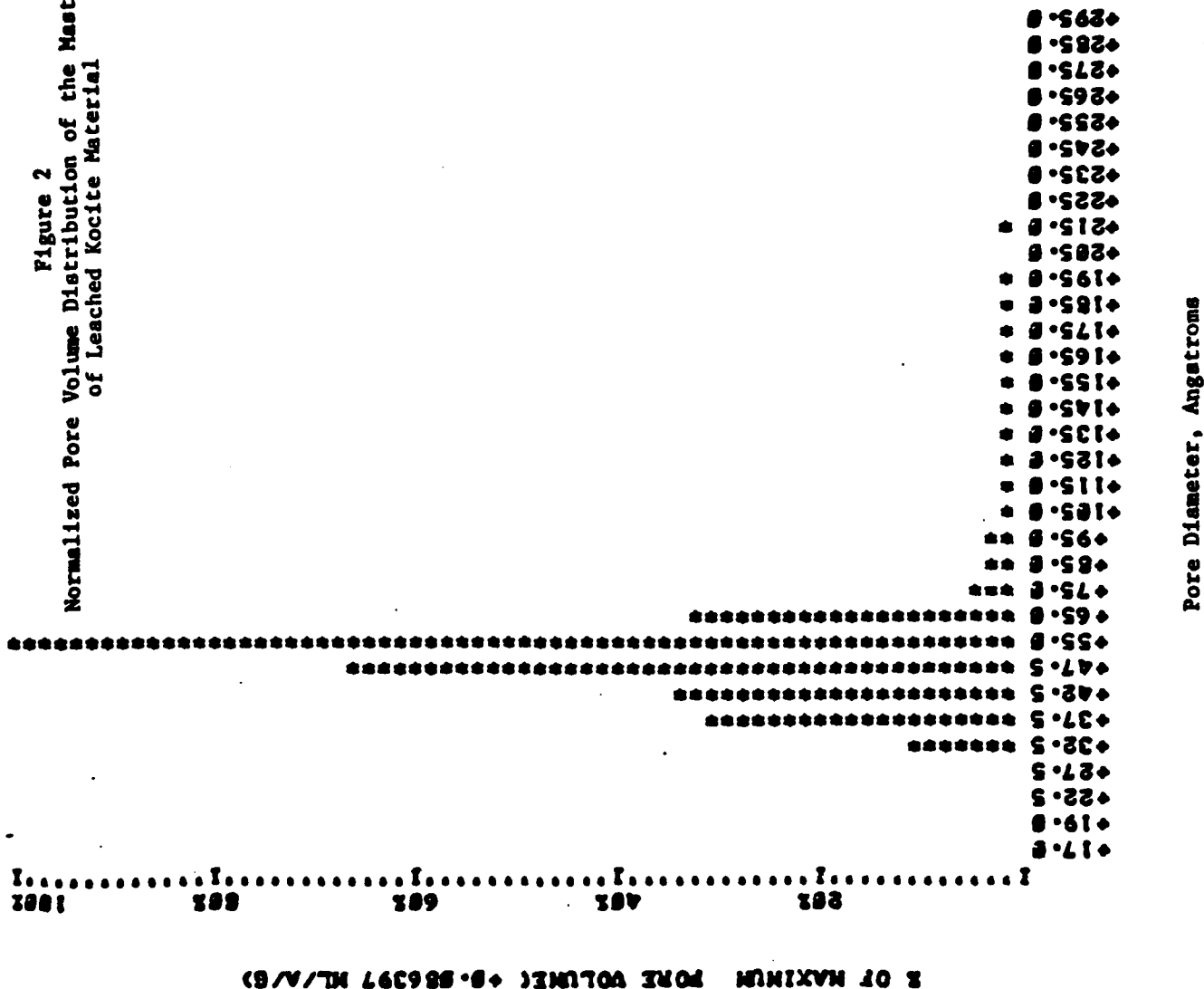


Figure 3
Normalized Pore Volume Distribution of the Support for Catalysts 6a and 6b

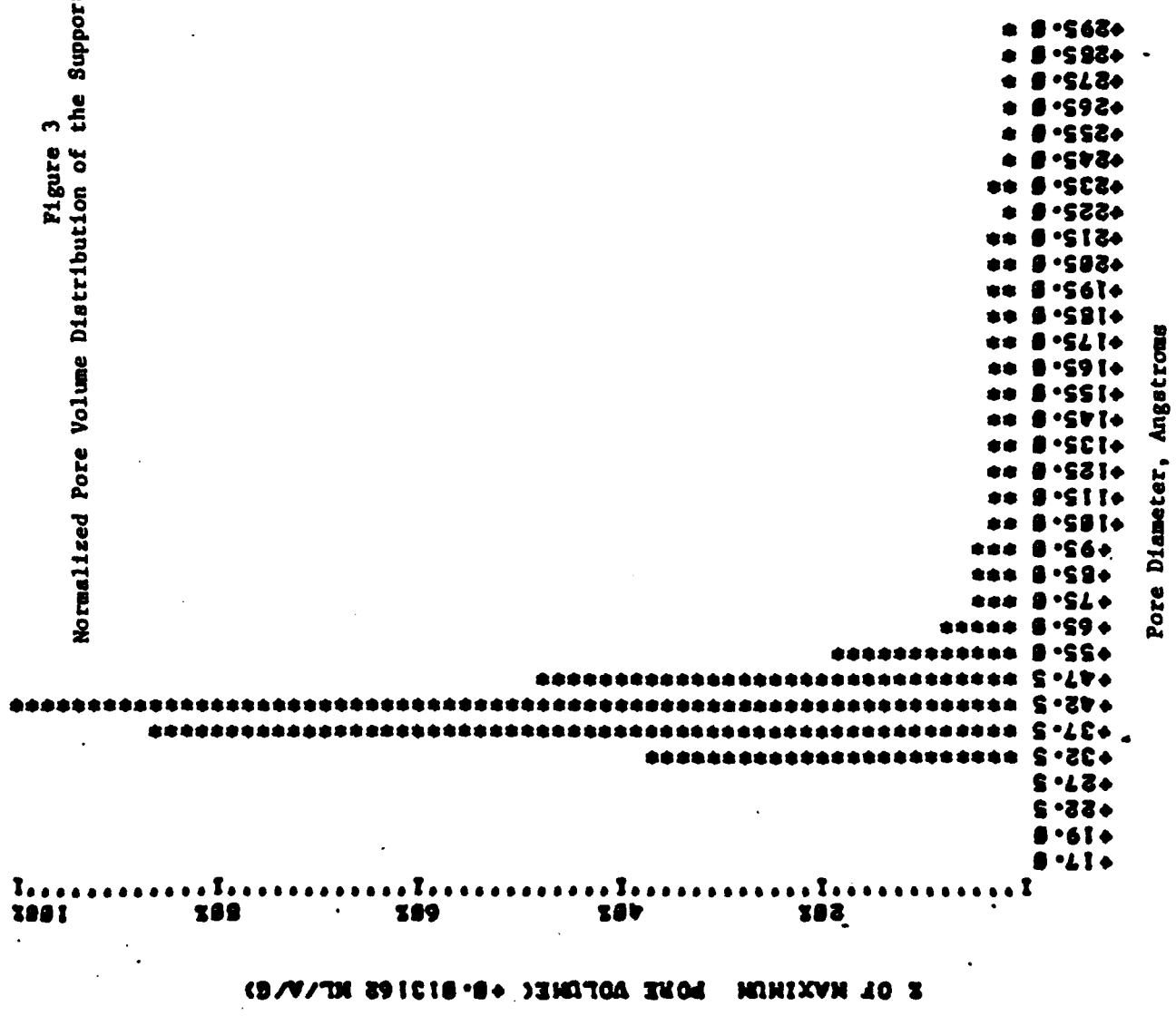
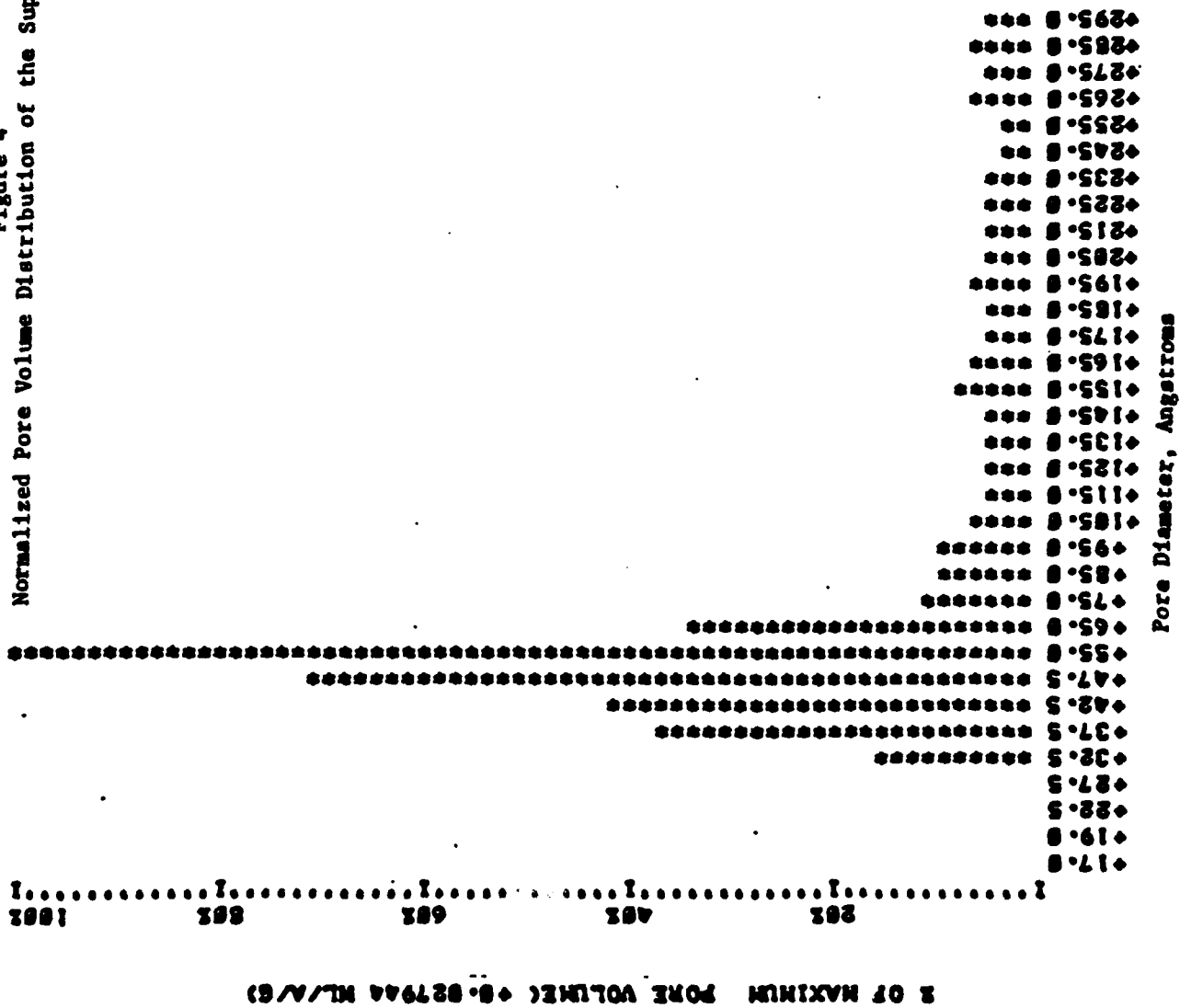


Figure 4
Normalized Pore Volume Distribution of the Support for Catalyst 4



IV. KOCITE ELECTROCATALYST AGING TEST RESULTS AND DISCUSSIONS

4.1 Aging Tests

The catalysts were aged in potentiostated half cells to test for catalytic metal surface area retention. The pattern of tests is listed in Table IV. The column "Cells" lists the number of cells successfully operated at each condition. Part 1 of the program consisted initially of the preparation of the standard catalyst and seven catalyst variations. Preparation of Catalyst 9 was added for testing by Energy Research Corp., but was not tested in this program. Later, three catalysts were added by impregnating three of the previously prepared catalysts with vanadium. Preliminary aging tests were carried out on the standard catalyst, and then eight of the variations were tested in two cells for 100 and 500 hours each at 190°C, potentiostated at 800 mV. Catalysts 2 and 7 were not tested because of the addition of the more important Pt-V alloy catalysts. In Part 2 of the program, Catalysts 3b-1 and 8b-1 were selected for further testing for reasons discussed in the next section. Catalysts 3b-2 and 8b-2 were prepared to be identical to Catalysts 3b-1 and 8b-1 and tested at 190°C for 100 and 500 hours at either 700 or 800 mV. Five cells were operated at each condition for each catalyst.

Table IV
Electrocatalyst Aging Test Conditions

- 190°C -

<u>Catalyst Number</u>	<u>Potentiostated Voltage (mV)</u>	<u>Time (h)</u>	<u>Cells</u>
1	700	100	4
	800	100	4
	700	500	2
	800	500	4
3a	800	100	1
	800	500	2
3b-1	800	100	1
	800	500	2
3b-2	700	100	5
	800	100	5
	700	500	5
	800	500	4
4	800	100	1
	800	500	2
5	800	100	2
	800	500	2
6a	800	100	1
	800	500	1
6b	800	100	1
	800	500	2
8a	700	100	2
	800	100	2
	700	500	1
	800	500	2
8b-1	800	100	2
	800	500	1
8b-2	700	100	4
	800	100	5
	700	500	5
	800	500	4

Catalysts 1, 3b-2, 8a, and 8b-2 were aged under the same conditions at 700 mV.

The results of X-ray diffraction analysis for platinum and Pt-V alloy surface areas are listed, for each cell tested, in the Appendix. These results have been corrected for any metals loss. Table V summarizes the metals retention of the aged catalysts. Table VI and Figures 5, 6, and 7 summarize the catalytic metal surface area retention results of the aged catalysts. These results will be discussed in the next section.

4.2 Discussion

The objectives of this program were to obtain Kocite electrocatalysts that have a better initial catalytic metal surface area and surface area retention than present state-of-the-art H_3PO_4 electrocatalysts. The aging tests were carried out to determine which catalyst modifications would lead to improved Kocite electrocatalyst stability in long term fuel cell operation.

The UOP experimental impregnation and the impregnation by the outside company both produced catalysts with higher initial platinum surface area than the PDD impregnation of the standard catalysts. The experimental impregnation on the heat treated support for Catalyst 6a gave a lower surface area than on the standard support for Catalyst 3a. Catalyst 5 on the oxidized support had a lower initial platinum surface area than the standard catalyst, though each was impregnated with PDD. The platinum-vanadium alloy catalysts aged in Part 1 of the program, Catalysts 3b-1, 6b, and 8b-1, had alloy surface areas similar to the platinum surface areas of the platinum catalysts from which they were made. The platinum-

Table V

Representative Catalytic Metal Content of Aged Electrocatalysts

<u>Catalyst</u>	<u>Time (h)</u>	<u>Potentiostated Voltage (mV)</u>	<u>Wt-% Pt</u>	<u>Wt-% V</u>
1	Fresh		9.9	-
	100	700	10.3	-
	100	800	10.3	-
	500	700	10.4	-
	500	800	10.6	-
3a	Fresh		10.5	-
	100	800	10.7	-
	500	800	10.7	-
3b-1	Fresh		10.8	0.76
	100	800	11.4	0.17
	500	800	10.5	0.10
3b-2	Fresh		11.0	1.20
	100	700	10.8	0.19
	100	800	10.8	0.14
	500	700	10.7	0.20
	500	800	10.7	0.14
4	Fresh		9.2	-
	100	800	10.1	-
	500	800	5.2	-
5	Fresh		9.8	-
	100	800	10.2	-
	500	800	10.3	-
6a	Fresh		10.1	-
	100	800	7.0	-
	500	800	2.3	-
6b	Fresh		9.5	0.79
	100	800	0.69	0.01
	500	800	8.3	0.07
	500	800	0.66	0.02
8a	Fresh		10.4	-
	100	700	10.4	-
	100	800	10.6	-
	500	700	10.7	-
8b	Fresh		10.8	0.95
	100	800	10.8	0.23
	500	800	11.2	0.16
8b-2	Fresh		11.4	0.90
	100	700	11.0	0.19
	100	800	11.0	0.16
	500	700	11.0	0.14
	500	800	10.7	0.14

Table VI

Summary of Catalytic Metal Surface Areas of Aged Kocite Electrocatalysts

<u>Catalyst*</u>	<u>Potentiostated Voltage</u>	<u>S (m²/g) Fresh Catalyst</u>	<u>S (m²/g) Aged Catalyst</u>	
			<u>100 h</u>	<u>500 h</u>
1	700	109	70	63
	800		72	54
3a	800	134	68	52
3b-1	800	135	73	43
3b-2	700	103	82	80
	800		78	64
4	800	138	112	29
5	800	99	84	50
6a	800	119	59	29
6b	800	123	9	21
8a	700	134	85	76
	800		74	52
8b-1	800	125	76	48
8b-2	700	107	74	71
	800		77	65

*3b-1, 3b-2, 6b, 8b-1, and 8b-2 are Pt-V Alloy Catalysts

Figure 5
Platinum Surface Areas of Aged Platinum Electrocatalysts Potentiostated at
800mV vs. NHE

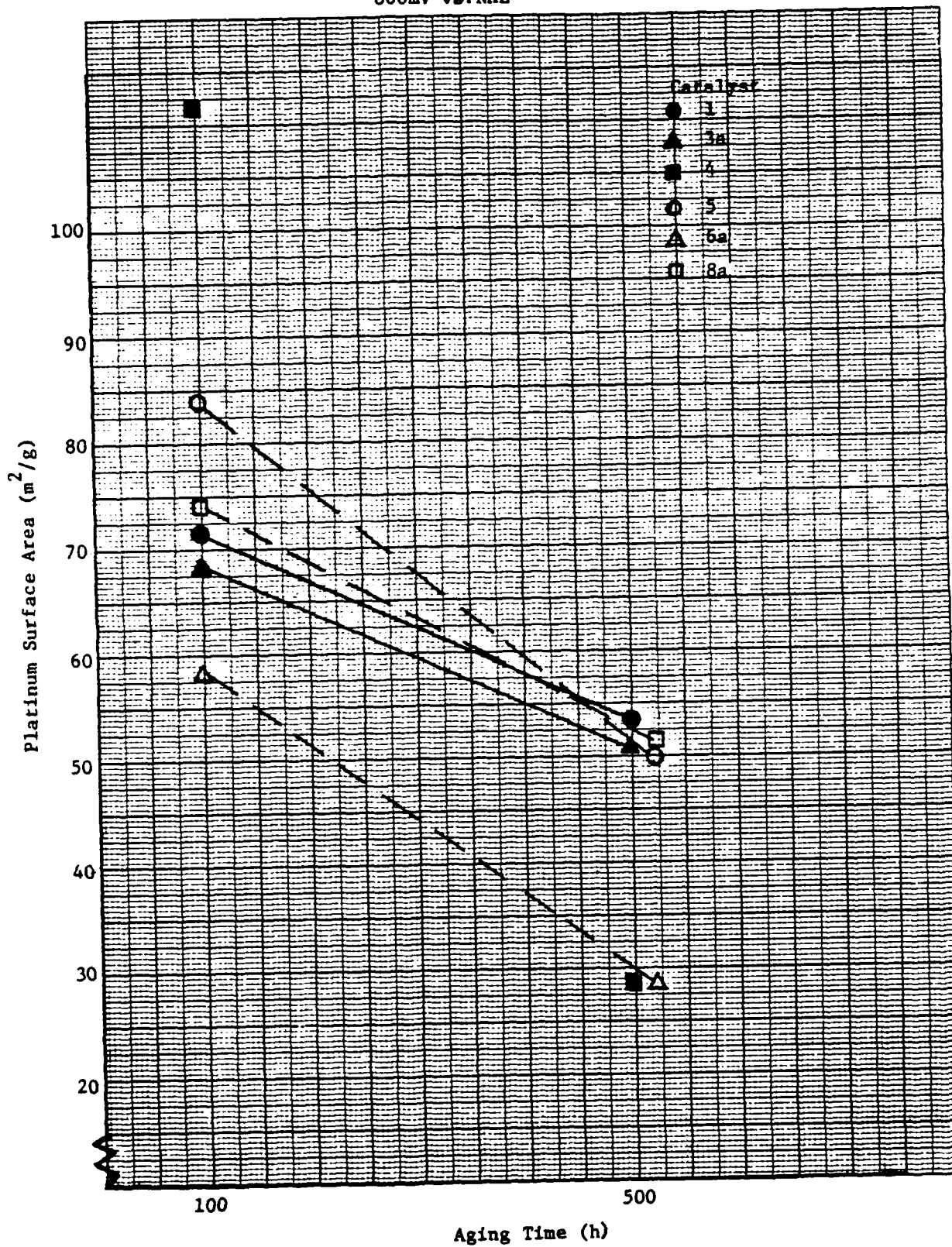


Figure 6
Alloy Surface Areas of Aged Pt-V Alloy Electrocatalysts Potentiostated
at 800mV vs. NHE

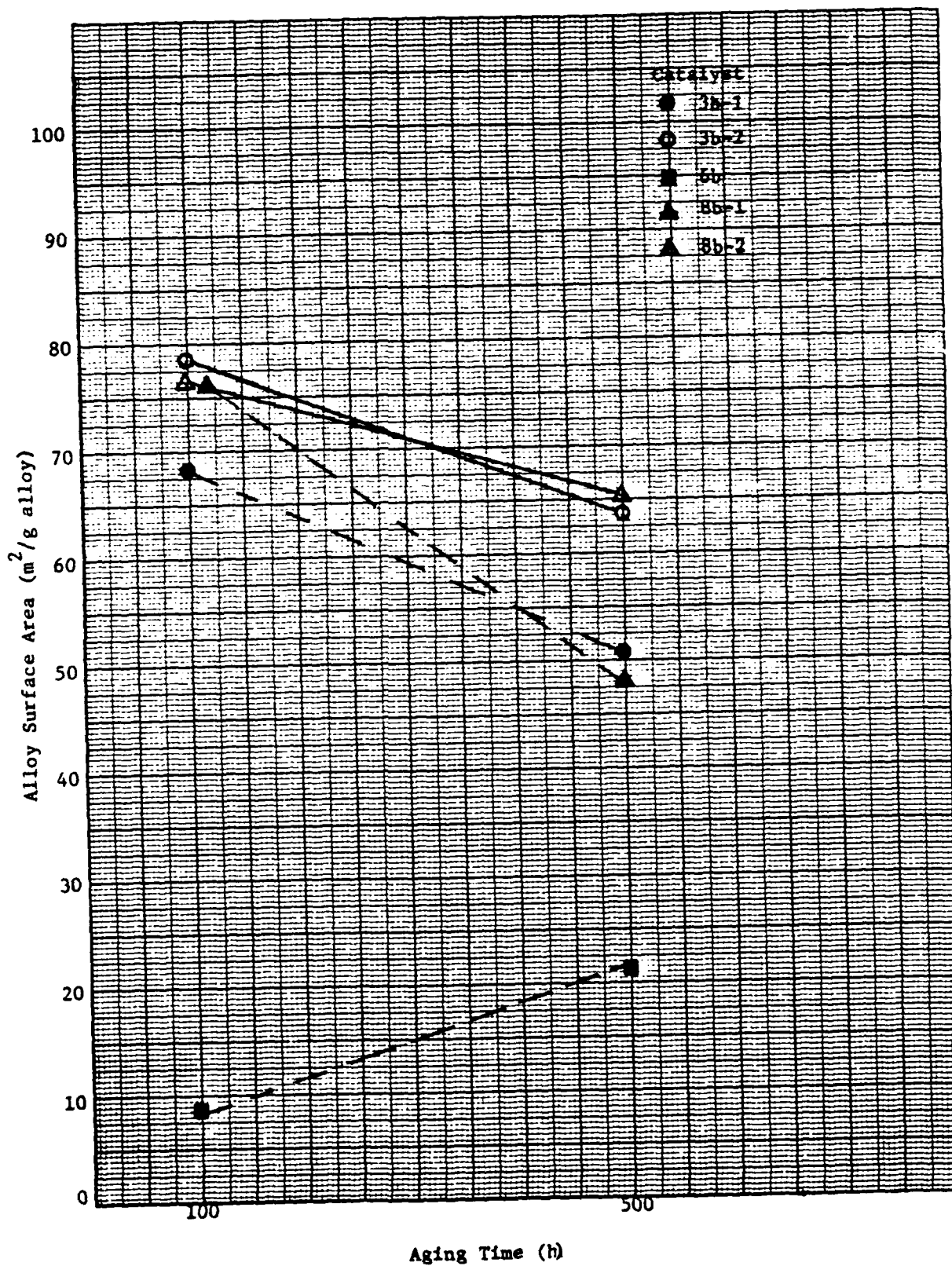
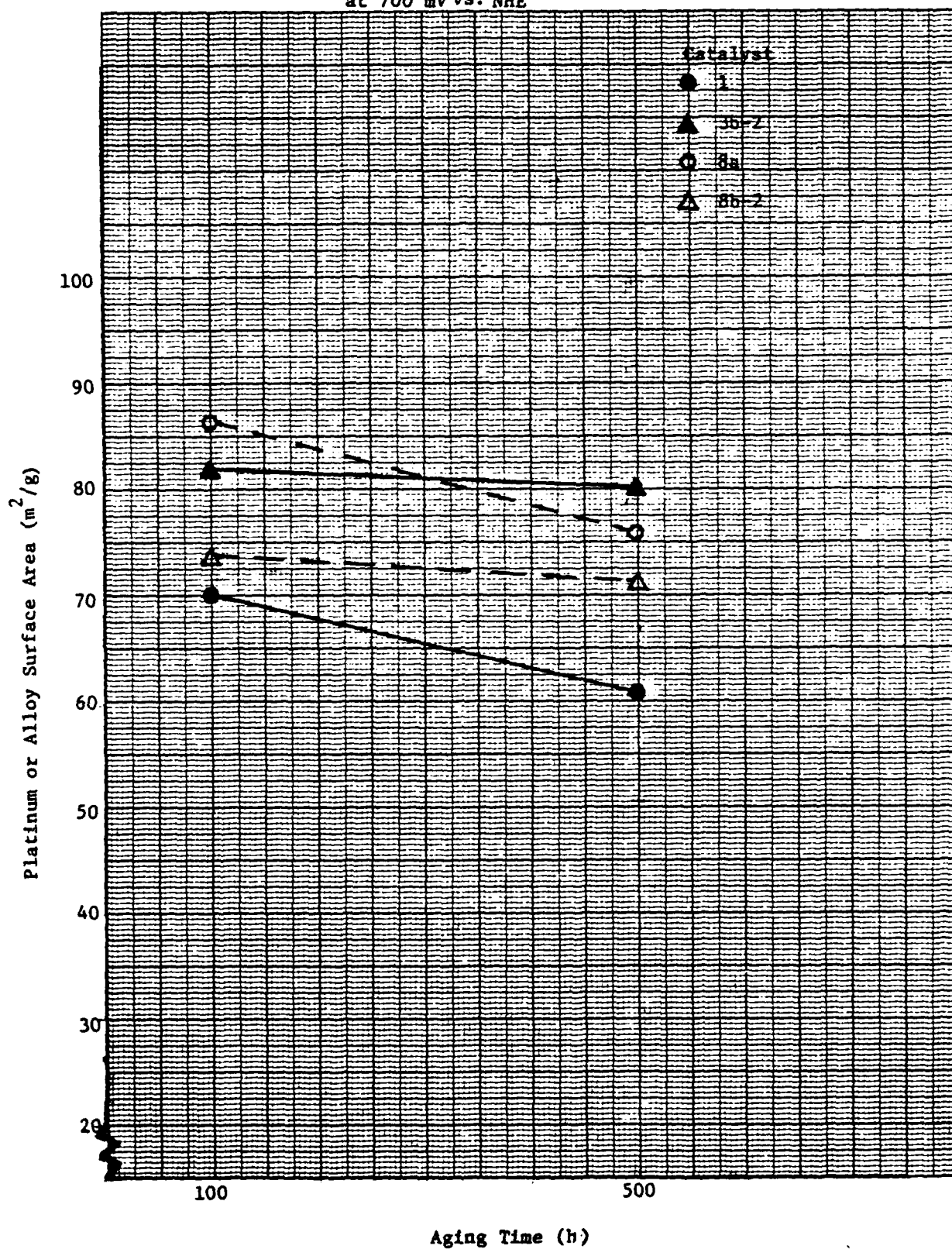


Figure 7
Platinum and Pt-V Alloy Surface Areas of Aged Electrocatalysts Potentiostated
at 700 mV vs. NHE



vanadium catalysts tested in Part 2 of the program, Catalysts 3b-2 and 8b-2, appear to have lower initial surface areas than Catalysts 3b-1 and 8b-1, however, Catalysts 3b-2 and 8b-2 were prepared with better understanding of the vanadium-complex decomposition technique. The higher surface area of catalysts, 3b-1 and 8b-1 may derive from broadening of the X-ray diffraction line because of a less uniform alloy composition rather than from a smaller average particle size.

The results of the preliminary tests at 800 mV indicate that the platinum catalysts, 1, 3a, 5, and 8a, have the same platinum surface area retention at 500 hours, as shown in Figure 5. Catalysts 1, 3a, and 8a were produced with three different impregnation techniques on the 3971-90L support. The support for Catalyst 5 had an oxidation treatment before the platinum was impregnated by the same technique as for Catalyst 1. Although the impregnation variations produce starting platinum surface areas which range from 99 m²/g for Catalyst 5 to 135 m²/g for Catalyst 8a, it appears that the platinum surface area retention is very similar for these catalysts after 500 hours of aging. In a previous study,² 5 and 15 wt-% Pt catalysts appeared to retain ~10 m²/g greater area at 500 hours than the presently tested catalysts. However, the previous results were obtained with catalysts prepared using different impregnation techniques and somewhat different test conditions.

Catalyst 4 was made on a support prepared using the Alon substrate, and Catalyst 6a used a heat treated support. Both had low platinum surface area retention due to platinum loss. Catalyst 4 retained a very high platinum surface area (112 m²/g) at 100 hours, but only had 50% of its platinum loading remaining at 500 hours. Catalyst 6a had poor platinum retention at both 100 and 500 hours.

The initial aging tests of the Pt-V alloy catalysts failed to confirm the stability improvement indicated from the earlier studies.² As shown in Figure 6, at 500 hours the alloy surface area retention of Catalyst 8b-1 was slightly below that of the standard catalyst and for Catalyst 3b-1 was $\sim 10 \text{ m}^2/\text{g}$ below that of the standard catalyst. Both catalysts appeared to retain their platinum loading, but only retained $\sim 15\%$ of their vanadium loading. The Pt-V alloy catalyst on the heat treated support, Catalyst 6b, had very little platinum or vanadium retained, even after only 100 hours.

The data for Catalysts 1 and 8a aged at 700 mV (Figure 7) do show a difference between the two catalysts at both 100 and 500 hours. Catalyst 8a retains a higher platinum surface area than Catalyst 1 under these milder aging conditions.

In Part 2 of the test program, the platinum-vanadium alloy catalysts, 3b-2 and 8b-2, were prepared and tested more fully than in Part 1. It was determined that difficulties encountered during decomposition of the vanadium complex could be avoided, and previous studies^{2,3} had indicated that the results from Part 1 might be anomalous. Since no catalysts showed a significant improvement over the standard catalysts, it was decided to use the further testing to reexamine the results on the Pt-V alloy catalysts. As is shown by the data in Table VI and Figures 6 and 7, retesting with more cells showed Catalysts 3b-2 and 8b-2 to have better alloy surface area retention, particularly at 500 hours. Within the error of the measurement both samples have the same alloy surface area retention at 800 mV. At 700 mV the $\sim 10 \text{ m}^2/\text{g}$ alloy surface area difference in the fresh catalysts is maintained after aging in the milder conditions. For Catalyst 8b-2, the values for aging at 700 mV compared with 800 mV after 100 hours are the same within the experimental error. It appears that greater care in the

vanadium complex decomposition for Part 2 has eliminated the inconsistency in the Pt-V alloy results in Part 1 of this study.

V. CONCLUSIONS

- A. Kocite electrocatalysts have been prepared by several impregnation techniques. Variations of the impregnation techniques used to prepare Kocite electrocatalysts have been shown to produce differing initial platinum surface areas for the catalysts. The UOP experimental colloidal impregnation and one done by an outside company both provide higher initial platinum surface areas than does the platinum diamine dinitrite impregnation of the standard Kocite electrocatalyst. However, after aging for 100 and 500 hours at 190°C and 800 mV vs. NHE, these initially higher platinum surface areas did not result in higher surface area retention when compared with the standard catalyst formulation. These results along with the results of previous studies imply that for fuel cells operated at high cell voltages, variation of the Kocite electrocatalyst impregnation technique to maximize the initial platinum surface area would not be expected to significantly improve long term fuel cell performance.
- B. High temperature heat treatment of the leached Kocite support leads to an increased loss of the catalytic metals on aging under the test conditions used in this study, though it probably stabilizes the support to carbon corrosion (oxidation).
- C. A partial oxidation of the leached Kocite support surface before impregnation does not appear to improve platinum surface area retention under these test conditions.

- D. Alon-based Kocite electrocatalysts do not appear to retain platinum as well as the standard, Hydral-based Kocite electrocatalyst.
- E. The results obtained with Kocite electrocatalysts aged at 700 mV vs. NHE were substantially different than those obtained at 800 mV. In particular, at 700 mV, platinum surface area differences present in the fresh Kocite electrocatalysts appear to be maintained after 500 hours of aging at 190°C in H_3PO_4 . In contrast, the results obtained at 800 mV indicate that any initial platinum surface area differences between Kocite electrocatalysts should be minimized after 500 hours of operation.
- F. The Pt-V alloy Kocite electrocatalysts made using the standard leached Kocite support material showed better alloy surface area retention than the pure platinum Kocite electrocatalysts, particularly after aging for 500 hours. Due to their superior alloy surface area retention, tests should be performed with the Pt-V alloy Kocite electrocatalysts in actual H_3PO_4 fuel cells to determine their long term performance in more realistic tests.

APPENDIX

Catalytic Metal Surface Area Retention Data for Aged Electrocatalysts

Catalyst 1

3971-90A-4

Pt Surface Area, Fresh Catalyst = 109 m²/g

<u>Aging Conditions</u>	<u>Remaining Pt Surface Area (m²/g)</u>
100 h, 190°C, 700 mV	69
	67
	71
	73
100 h, 190°C, 800 mV	71
	70
	72
	73
500 h, 190°C, 700 mV	61
	65
500 h, 190°C, 800 mV	56
	49
	58
	52

Catalyst 3a

3971-90A-5

Pt Surface Area, Fresh Catalyst = 134 m²/g

<u>Aging Conditions</u>	<u>Remaining Pt Surface Area (m²/g)</u>
100 h, 190°C, 800 mV	68
500 h, 190°C, 800 mV	43
	62

Catalyst 3b-1

3971-90AV-5

Pt-V Alloy Surface Area, Fresh Catalyst = 135 m²/g Alloy

<u>Aging Conditions</u>	<u>Remaining Alloy Surface Area (m²/g Alloy)</u>
100 h, 190°C, 800 mV	73
500 h, 190°C, 800 mV	33 53

Catalyst 3b-2

3971-90AV-5-2

Pt-V Alloy Surface Area, Fresh Catalyst = 103 m²/g Alloy

<u>Aging Conditions</u>	<u>Remaining Alloy Surface Area (m²/g Alloy)</u>
100 h, 190°C, 700 mV	91 85 76 86 72
100 h, 190°C, 800 mV	74 89 79 81 66
500 h, 190°C, 700 mV	78 92 73 74 82
500 h, 190°C, 800 mV	56 69 61 70

Catalyst 4
3971-104A

Pt Surface Area, Fresh Catalyst = 138 m²/g

<u>Aging Conditions</u>	<u>Remaining Pt Surface Area (m²/g)</u>
100 h, 190°C, 800 mV	112
500 h, 190°C, 800 mV	29 29

Catalyst 5
3971-90A-6

Pt Surface Area, Fresh Catalyst = 99 m²/g

<u>Aging Conditions</u>	<u>Remaining Pt Surface Area (m²/g)</u>
100 h, 190°C, 800 mV	85 83
500 h, 190°C, 800 mV	43 56

Catalyst 6a
3971-90A-1-2500°C

Pt Surface Area, Fresh Catalyst = 119 m²/g

<u>Aging Conditions</u>	<u>Remaining Pt Surface Area (m²/g)</u>
100 h, 190°C, 800 mV	59
500 h, 190°C, 800 mV	29

Catalyst 6b
3971-90AV-1-2500°C
Pt-V Alloy Surface Area, Fresh Catalyst = 123 m²/g Alloy

<u>Aging Conditions</u>	<u>Remaining Alloy Surface Area (m²/g)</u>
100 h, 190°C, 800 mV	9
500 h, 190°C, 800 mV	32 10

Catalyst 8a
3971-90A-12
Pt Surface Area, Fresh Catalyst = 134 m²/g

<u>Aging Conditions</u>	<u>Remaining Pt Surface Area (m²/g)</u>
100 h, 190°C, 700 mV	82 89
100 h, 190°C, 800 mV	65 82
500 h, 190°C, 700 mV	76
500 h, 190°C, 800 mV	58 45

Catalyst 8b-1
3971-90AV-2
Pt-V Alloy Surface Area, Fresh Catalyst = 125 m²/g Alloy

<u>Aging Conditions</u>	<u>Remaining Alloy Surface Area (m²/g)</u>
100 h, 190°C, 800 mV	75 76
500 h, 190°C, 800 mV	48

Catalyst 8b-2
3971-90AV-2-2
Pt-V Alloy Surface Area, Fresh Catalyst = 107 m²/g Alloy

<u>Aging Conditions</u>	<u>Remaining Alloy Surface Area (m²/g)</u>
100 h, 190°C, 700 mV	70
	73
	77
	74
100 h, 190°C, 800 mV	72
	76
	79
	79
	78
500 h, 190°C, 700 mV	72
	75
	69
	69
	71
500 h, 190°C, 800 mV	72
	62
	69
	57

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